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Title page

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Title: **On the application of ICP-MS techniques for measuring U and Pu: a Nordic inter-laboratory comparison exercise**

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**On the application of ICP-MS techniques for measuring
uranium and plutonium: a Nordic inter-laboratory
comparison exercise**

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Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) techniques are widely used for
determination of long-lived radionuclides and their isotopic ratios in the nuclear fields.
Uranium (U) and Pu (Pu) isotopes have been determined by many researchers with ICP-
MS due to its relatively high sensitivity and short measurement time. In this work, an

inter-laboratory comparison exercise among the Nordic countries was performed, focusing on the measurement of U and Pu isotopes in certified reference materials by ICP-MS. The performance and characters of different ICP-MS instruments are evaluated and discussed in this paper.

Keywords

ICP-MS, Pu, U, NBL CRM-103A, IAEA-384

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) was developed by combining an inductively coupled plasma source at atmospheric pressure with mass spectrometry. ICP-MS has advantages of relatively low operational cost, easy sample introduction and high sample throughput. Since its first commercial introduction in 1983, ICP-MS has become widely used for determination of radionuclides (e.g., actinides) and their isotopic ratios in the fields related to environmental monitoring, nuclear waste disposal and management, radioecology and tracer studies, nuclear forensics and nuclear emergency preparedness.[1–13] Many researchers have applied ICP-MS for the determination of uranium (U) and plutonium (Pu) isotopes, because of its relatively high sensitivity and high sample throughput due to the short measurement time needed compared to traditional radiometric techniques.[14–23]

There are several types of ICP-MS instruments commercially available, including quadrupole ICP-MS (ICP-QMS), single- or double-focusing sector field ICP-MS (ICP-SFMS), multi-collector ICP-MS (MC-ICP-MS), and recently introduced triple quadrupole ICP-MS (ICP-QQQ). Each type of instrument has advantages and drawbacks with respect to the determination of U and Pu isotopes. ICP-QMS, ICP-SFMS and ICP-QQQ are single collector inductively coupled mass spectrometers based on different technical principles. The basic difference between operating principles of single collector and multi-collector ICP-MS instruments is the sequential measurement of multiple

isotopes by one detector vs. the simultaneous measurement of isotopes at multiple detectors, respectively. Owing to its possibility of simultaneous detection, multi-collector ICP-MS is outstanding regarding expanded uncertainty of isotope ratio determination. However, depending on the application and the need of precision, single collector or quadrupole ICP-MS may give sufficiently good results [24].

Among the Nordic countries, there are probably 20 ICP-MS facilities, which are currently applied for measuring radionuclides and their isotopic ratios. With different application purposes and technical background of the analysts, each ICP-MS laboratory has different set-ups and experiences in instrumental operation. Aiming to prompt knowledge sharing among different ICP-MS laboratories, and thus achieve more efficient application of ICP-MS techniques, an inter-laboratory comparison exercise was performed during 2016. The exercise focused on the determination of U and Pu isotopes in certified reference materials with the application of different ICP-MS instruments. It consisted of two aspects: 1) ICP-MS measurement for U isotopic ratios ($^{234}\text{U}/^{235}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$); 2) ICP-MS measurement for Pu isotopes (^{239}Pu and ^{240}Pu) concentrations and isotopic ratio. The inter-comparison results were evaluated and discussed to shed some light on the analytical feature of different ICP-MS instruments and the effect of operational conditions/auxiliary devices on the ICP-MS performance.

Experimental

Materials

A certified reference material NBL CRM 103-A Pitchblende Ore – Silica Mixture Uranium Standard (U 0.04992 ± 0.00078 Wt.%) from New Brunswick Laboratory (NBL) was used in the inter-comparison exercise to perform the U isotopic ratios ($^{234}\text{U}/^{235}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$) measurement. According to the certificate, the material was prepared by milling and blending NBL CRM 6-A Pitchblende Ore (67.91 ± 0.05 Wt.% U_3O_8) with silica (99.9% SiO_2) to obtain a uniform mixture of desired U concentration. NBL CRM 103-A is not certified for U isotope ratios, but the material has natural U

isotopic composition, hence the IUPAC observed range of natural variations for U [25] has been used in this inter-comparison.

Another certified reference material IAEA-384 Fangataufa Lagoon sediment was used for the determination of the concentrations of ^{239}Pu and ^{240}Pu and their isotopic ratio. This material was collected by IAEA-MEL in July 1996 in Fangataufa Lagoon (French Polynesia), where nuclear weapon testing had been carried out.

Sample preparation for measuring U isotope ratios

Details of the sample preparation procedure for U isotopic ratios measurement are summarized below. Generally, a certain amount of NBL CRM 103-A reference material was dissolved using mineral acids (i.e., HF, HNO_3 and HCl). After suitable dilution with diluted HNO_3 , the sample was measured by different ICP-MS instruments in each laboratory.

At Lab A, 50-100 mg of NBL CRM 103-A reference material was dissolved using about 2 ml of concentrated HF and 2 ml of concentrated HNO_3 with addition of 200 μl of concentrated HCl. Thereafter the sample solution was diluted with 0.3-0.5 M HNO_3 to an appropriate concentration.

At Lab B, 100 mg of NBL CRM 103-A reference material was dissolved in 2 ml of concentrated HF, 2 ml concentrated HNO_3 and 200 μl of concentrated HCl. Thereafter the sample solution was diluted in 0.28 M HNO_3 to appropriate concentration.

At Lab C, 50 mg of NBL CRM 103-A reference material was dissolved using a microwave-assisted digestion system with 2 ml of concentrated HF and 2 ml of concentrated HNO_3 in closed Teflon vessels at 600 W RF power for 25 minutes. Digests were evaporated to dryness and re-dissolved in 0.3 M HNO_3 . Thereafter the sample solution was diluted in 1.4 M HNO_3 to appropriate concentration.

At Lab D, 2 mg of NBL CRM 103-A reference material was weighed to a Teflon beaker and 5 ml of concentrated HNO_3 (super pure) was added. The mixture was nearly boiled

for 2 hours. The solution was filtered through a membrane filter (Acrodisc® Syringe Filter, 0.2 µm Supor® Membrane, Pall Life Sciences) and diluted to 100 ml with H₂O.

At Lab E, the sample was dissolved only with 0.1 M HNO₃ in the preliminary test. However, the sample solution obtained was not clear, and analytical result was very unstable with high deviation, indicating that the solution was inhomogeneous. Afterwards, the sample was dissolved with 0.5 M HNO₃ + 0.25% (v/v) HF, wherein clear solutions were obtained.

At Lab F, 80 mg of NBL CRM 103-A reference material was digested in PTFE tubes with 2.5 ml of concentrated HNO₃ for 40 minutes at 260 °C in an UltraWave from Milestone. The samples were diluted to 25 ml with de-ionized water after digestion.

Sample preparation for measuring Pu isotopes

For ²³⁹Pu and ²⁴⁰Pu concentration and isotopic ratio measurement, two approaches were used for the sample preparation: 1) centralized sample preparation and dispatching the purified Pu solution to each laboratory for direct ICP-MS measurement; 2) dispatching the raw reference material IAEA-384 and performing independent sample preparation in individual laboratory. In general, the radiochemical methods used for the determination of Pu in the raw IAEA-384 material were based on sample pre-treatment followed by extraction chromatographic separation (two labs used TEVA, one used tandem UTEVA + TRU and one used UTEVA column) and ICP-MS measurement.

Pre-purification of IAEA-384 for Pu measurement. Pu contained in IAEA-384 material was pre-separated at Lab A and distributed to participating institutes for measurement. The chemical separation procedure for purification of Pu at Lab A is summarized as follows. 2 g of IAEA-384 sediment was spiked with 0.2528g of 0.1037 Bq/kg ²⁴²Pu tracer and dissolved directly with 20 ml of 8 M HNO₃. A 4 ml of anion exchange column (AG 1×4, 50-100 mesh) was packed and preconditioned with 20 ml of 8 M HNO₃. The dissolved sample solution was loaded onto the column, and the column was washed with 60 ml of 8 M HNO₃ followed by 40 ml of 9 M HCl. The Pu was eluted with 50 ml of 0.5 M HCl and the eluate was evaporated to dryness. The Pu residue was

dissolved with 12 ml of 0.5 M HNO₃, and each 2 ml of aliquot was transferred to a scintillation vial and delivered to ICP-MS measurement in each laboratory.

Radiochemical separation for IAEA-384. Raw IAEA-384 reference material was also processed in participating laboratories to perform the inter-comparison of radiochemical analysis for Pu determination. The radiochemical separation procedures used in this inter-comparison are summarized below.

At Lab A, 0.2 g of IAEA-384 reference material was spiked with 0.1g of 0.1037 Bq/kg ²⁴²Pu tracer and digested with 40 ml *aqua regia* at 200 °C for 2 hours. After filtration, 1 mg of Fe was added to form Fe(OH)₃ co-precipitation with the addition of NH₃ to pH 8-9. After centrifugation, the residue was dissolved with 2 ml concentrated HCl and diluted to 100 ml. In total of 300 mg of K₂S₂O₅ was added with stirring for 20 min. to reduce Pu to Pu(III). NH₃·H₂O was added to adjust the sample to pH 8-9 and the precipitate was centrifuged. 3 ml of concentrated HNO₃ was added to dissolve the residue and the sample was finally adjusted to 3 M HNO₃ for chromatographic purification. 2 ml of TEVA (100-150 µm) column was packed and preconditioned with 20 ml of 3 M HNO₃. The dissolved sample solution was loaded onto the TEVA column, and the column was washed with 60 ml of 8 M HNO₃ followed by 40 ml of 9 M HCl. The Pu was eluted with 50 ml of 0.5 M HCl and the eluate was evaporated to dryness. The Pu residue was dissolved with 5 ml of 0.5 M HNO₃ and measured with an ICP-QQQ instrument.

At Lab B, the reference material IAEA-384 was first checked for moisture content. 1 g of IAEA-384 sediment was mixed with 3 g lithium metaborate (LiBO₂, Claisse, ultra-pure grade, Gammadata, Uppsala, Sweden) and thereafter spiked with about 10 pg of ²⁴²Pu (NIST SRM 4334G). The sample mixture was first pre-oxidized at 650°C for 1 hour prior to fusion for 15 minutes at 1050°C. The melt was allowed to cool before mixing with 100 ml of 1.4 M HNO₃ and thereafter the melt was dissolved under stirring and heat. When dissolved, PEG2000 was added to a concentration of 0.0002 M and thereafter the sample volume was evaporated to half the volume, leading to a sample matrix of 2.8 M HNO₃. The sample was left over night to allow silica to flocculate and thereafter the sample was filtrated using filter paper (Munktell filter paper No. 00M). The sample filtrate was

heated to 90°C and thereafter 375 mg of $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added. After cooling, 900 mg of NaNO_2 was added to assure that all Pu was oxidized to Pu(IV). 2 ml TEVA (Triskem) columns were packed in-house in 3 ml cartridges (Isolute reservoir 3 ml, Biotage, Uppsala, Sweden). 20 μm polyethylene frits (Biotage) were used to keep the TEVA resin in the reservoir. The column was pre-conditioned with 5 ml of 3 M HNO_3 and then the sample was added. The column was rinsed with 10 ml of 3 M HNO_3 , followed by 10 ml of 9 M HCl and 20 ml 3 M HNO_3 . Pu was eluted in 5 ml of 0.01% hydroxylethylidene diphosphonic acid (HEDPA, purum, Merck Millipore, Stockholm, Sweden) and measured with an ICP-SFMS instrument.

At Lab C, 0.25 g of IAEA-384 reference material was digested with a microwave-assisted digestion system using HNO_3 +HF mixture as described earlier for pre-treatment of NBL CRM 103-A. After evaporation, the sample was re-dissolved in 3M HNO_3 and then loaded on a pre-packed 2 ml UTEVA column for Pu separation from matrix. The UTEVA column was washed by 12 ml of 3 M HNO_3 and 4 ml of 9.6 M HCl followed by Pu elution in 8 ml of 5 M HCl +0.05M oxalic acid. ^{242}Pu spike (NIST SRM 4334G) was used as a tracer of the entire procedure.

At Lab D, 1 g of IAEA-384 reference material was spiked with 26 mBq (177 pg) of ^{242}Pu as a tracer. The sample was dissolved with the mixture of concentrated HNO_3 (30 ml) and concentrated HCl (10 ml) on a hotplate for 6 hours. The sample solution was filtrated and evaporated to dryness. Radiochemical separation of Pu from the disturbing matrix and other radionuclides was performed according to the method described elsewhere [26]. In general, after dissolving the sample in 10 ml of 1 M $\text{Al}(\text{NO}_3)_3$ + 3 M HNO_3 , 2 ml of 0.6 M ferrous sulfamate solution and 150 mg of ascorbic acid were added. After 15 minutes, the sample solution was loaded into an UTEVA column (preconditioned with 5 ml of 3 M HNO_3). The UTEVA column was washed with 10 ml of 3 M HNO_3 . The effluent of the sample loading and washing solution were loaded onto a TRU column (preconditioned with 5 ml of 2 M HNO_3). The TRU column was washed with 5 ml of 2 M HNO_3 , 5 ml of 0.1 M NaNO_2 + 2 M HNO_3 , 3 ml of 0.5 M HNO_3 , 2 ml of 9 M HCl , 20 ml of 4 M HCl and 10 ml of 0.1 M HF + 4 M HCl , respectively. Pu was finally eluted with 10 ml of 0.1 M $\text{NH}_4\text{HC}_2\text{O}_4$ and evaporated to dryness. 2 ml of conc. HNO_3 was

added to the residue and re-evaporated into dryness. The separation procedure with UTEVA and TRU columns was repeated. After elution from TRU column, the ammonium oxalate solution containing Pu was evaporated into dryness with addition of a few drops of H₂O₂ and concentrated HNO₃. The residue was dissolved to 10 ml of 5 % HNO₃ and filtered through a membrane filter (Acrodisc® Syringe Filter, 0.2 µm Supor® Membrane, Pall Life Sciences). Blank samples were processed similarly with the sediment samples. Blank samples and acid blank of 5% HNO₃ were included to the measurement sample set.

At Lab F, 1 g of IAEA 384 was weighed directly in to a PTFE digestion tube and 12 mL of concentrated HNO₃ and 4 mL of 48 % (w/w) HF were added. 24.1 pg of ²⁴²Pu was added as a yield tracer. The samples were digested (UltraClave IV, Milestone Ltd) at a temperature of 260 °C for 40 minutes. After digestion, the samples were transferred to PTFE beakers and left to evaporate to dryness on a sand-bath. Matrix separation was performed according to the method described in [27]. The eluate from the separation was evaporated to dryness, and taken up in 7 ml of 0.8 M HNO₃ + 0.2 M HF for analysis. The pre-purified Pu sample was diluted in a ratio of 1:3 with 0.8 M HNO₃ + 0.2 M HF before analysis.

Instrumentation, measurement and calculations

Within this work, six Nordic laboratories participated in the inter-comparison exercise, where two ICP-QQQ, one MC-ICPMS and four ICP-SFMS instruments were employed for the U and Pu measurement. Table 1 summarizes the instrumentation conditions used in each laboratory.

Lab A: The instrumentation used throughout the work was an ICP-QQQ (Agilent 8800). Both U and Pu measurements, standard introduction system consisted of MicroMist nebulizer and Scott-type double pass spray chamber, together with Ni skimmer cone and x-lens were used. Typical sensitivity of the instrument is about 0.7 cps per ppq for ²³⁸U. The uptake of the sample was performed at a flow rate of 20 µL/min with a standard peristaltic pump equipped in the ICP-QQQ instrument. A ²⁴²Pu standard solution was diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL, USA). A 1000

ppm standard solution of U (Scientific Standards) was diluted to different levels of concentrations and used for calibration purposes. All standard solutions and samples were diluted to appropriate concentrations using high purity water and concentrated nitric acid.

For the measurement of U at Lab A, the instrument was controlled for mass bias using the standard solution NBL-112a with a concentration of 0.5 ppb. The major isotope ratio $n(^{235}\text{U})/n(^{238}\text{U})$ was determined in a sample diluted to achieve a maximum intensity of 1×10^6 counts/s at m/z 238. The minor isotope ratio $n(^{234}\text{U})/n(^{235}\text{U})$ was measured in a sample diluted to achieve an intensity of about 1×10^6 counts/s at m/z 235 and thereafter the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio was calculated from the ratios of $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{234}\text{U})/n(^{235}\text{U})$. For the measurement of Pu, a 0.5 M HNO_3 as a blank, ^{242}Pu (4.09 ppt) standard and ^{238}U (1ppb) standard was measured in parallel with the purified Pu fraction (in 0.5 M HNO_3). 1 ppb In (as InCl_3) was added into each sample and used as an internal standard to calibrate the efficiency of instrument. The signals at m/z 240 and 242 were corrected for contributions from blank levels and the signal at m/z 239 was corrected for contributions both from blank and ^{238}U . Mass bias correction was not performed for ^{239}Pu and ^{240}Pu , whereas average isotope ratios ($n=5$) of $n(^{239}\text{Pu})/n(^{242}\text{Pu})$ and $n(^{240}\text{Pu})/n(^{242}\text{Pu})$ were calculated based on the intensities measured by ICP-MS. Thereafter the activity concentrations of ^{239}Pu and ^{240}Pu in the raw sample were calculated by multiplying the total amount of ^{242}Pu tracer spiked in the sample with $^{239}\text{Pu}/^{242}\text{Pu}$ and $^{240}\text{Pu}/^{242}\text{Pu}$ isotopic ratios, respectively.

Lab B: The instrumentation used throughout the work was an ICP-SFMS (Element XR, Thermo Scientific, Bremen, Germany). For the Pu measurement, the retarding potential quadrupole lens of the ICP-SFMS was activated to reduce the peak tailing of the instrument, whilst for the U measurement the RPQ lens was inactivated. The instrument was tuned for maximum U intensity meanwhile keeping the U oxide formation as low as possible. The typical sensitivity is about 2 cps per ppq for ^{238}U with the RPQ lens inactivated. When using the instrument with the RPQ lens activated, the typical sensitivity is decreased by about 10%, see Table 1. The automatic dead time correction was disconnected as this correction was performed post-acquisition. The sample

introduction systems used consisted of a Conikal nebulizer, a Twister spray chamber, a standard torch and nickel cones (all from GlassExpansion, Melbourne, Australia).

For the determination of U and Pu at Lab B, the instrument was controlled for mass bias and spectral interference at m/z 239 from ^{238}U using the certified reference material IRMM-073/7 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium). IRMM-184 was used as a quality control sample. The raw data was extracted from the instrument to avoid non-linearity effects as published earlier [28] and data reduction thereafter was done off-line in order to correct detector dead time of the individual, averaged signal intensities. The detector dead time and its associated uncertainty, was determined to be 73.1 ± 1.4 ns, with the 70 ns nominal dead time setting on the ion detection board using IRMM-073/5 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium) by a method described by Appelblad and Baxter [29]. Following the dead time correction, the intensities were corrected for contributions from blank levels, and thereafter mass bias corrected ratios for $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$, $n(^{240}\text{Pu})/n(^{239}\text{Pu})$, $n(^{239}\text{Pu})/n(^{242}\text{Pu})$ and $n(^{240}\text{Pu})/n(^{242}\text{Pu})$ were calculated using the Russell equation [30]. For the separated Pu sample, the signal at m/z 239 was also corrected for contributions from ^{238}UH and peak tailing from ^{238}U prior to mass bias correction. All uncertainties were evaluated in accordance with ISO/GUM (1995) using the software GUM Workbench [32].

Lab C: An ICP-SF-MS (ELEMENT XR, Thermo Scientific) was used for both Pu and U measurement in this work. For the U ratio measurement, a dual spray chamber for signal stability improvement together with a Micromist nebulizer and standard cones were used. RPQ (Retarding Potential Quadrupole) lenses were activated to improve abundance sensitivity. This set-up offers a typical sensitivity of 1.2 cps per ppq for ^{238}U and $^{238}\text{U}/^{238}\text{U}^1\text{H}$ ratio of >60000. For the Pu isotope measurement, a desolvation sample introduction system (APEX) equipped with a PFA nebulizer and high efficiency skimmer cone was used. RPQ was also activated with a typical sensitivity of > 6 cps per ppq for ^{238}U . Standard solutions of U0002 CRM, IRMM-184, CRM130 and 1000-ppm U standard (Scientific Standards) were used for tailing and spectral interference corrections as well as for calibration purposes.

Mathematical corrections for $^{238}\text{U}^{\text{H}^+}$ and tailings were performed based on experimental factors deduced by analyzing U0002 CRM. Mass bias was assessed using IRMM-184 (natural U). Concentration was determined using external calibration with diluted CRM130 (Pu) and Scientific Standards 1000 ppm U solutions.

Lab D: Two ICP-MS instruments, a Nu Plasma Multi-Collector ICP-MS and a Nu AttoM Single-Collector ICP-MS (Nu Instruments Ltd., Wrexham, UK), were used in this inter-comparison. Limit of detection (LOD) was < 20 ppq for Pu and U before the sample measurements.

The analyses of U isotopes were carried out by using a Nu Plasma Multi-Collector ICP-MS at low mass resolution ($\Delta m/m = 400$). The U measurements were performed in dynamic mode and consists of 1 block of 12 integrations of 15s (2 cycles for the two isotopes ratio) and 1s (3 cycles for the tail corrections). A 5 min wash using HNO_3 (2%) has been used between U isotopes measurements. Two Faraday detectors have been used for ^{238}U and ^{235}U and one ion counter has been used for ^{234}U , ^{233}U and tail corrections in U isotope measurements. The samples have been standard bracketed using the NBL112a standard [33] in order to correct for mass fractionation and Faraday cup to ion counter gain. Peak tailing has been corrected using an exponential function after dynamic measurements at three different half-masses 232.5, 233.5 and 234.5 on the same ion counter used for the determination of ^{234}U and ^{233}U . The international U standard UO10 has been used for quality control at the beginning and at the end of each run. The measured $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios for that standard during analytical sessions were 0.00005436 ± 35 and 0.010149 ± 8 ($n = 4$), compared to respective values 0.00005448 ± 4 (reference value from [34]) and 0.010140 ± 10 (certified value).

The Nu AttoM Single-Collector ICP-MS instrument was used for the determination of ^{239}Pu and ^{240}Pu . The sample introduction system consisted of an autosampler, a peristaltic pump, a Meinhard nebulizer, nickel and sampler cones and a cyclonic spray chamber without cooling. In determination of ^{240}Pu and ^{239}Pu , the samples were bracketed using a CPITM single element solution of 1 ppb of U in 2% HNO_3 , meaning that the U standard solution was measured between every sample measurement. A blank has been measured

before every sample and standard. Analyses were performed in deflector jump mode using 80 sweeps of 500 cycles at low resolution. The isotopes of ^{238}U , ^{235}U , ^{239}Pu , ^{240}Pu , and ^{242}Pu , as well as half masses at 239.5 and 240.5 were measured. The dwell time was 1 ms for each isotope. Washing time was 120 s and a further 60 s of sample uptake was allowed before measurement started. The results have been calculated using an in house excel data reduction program. The natural ratio of $^{238}\text{U}/^{235}\text{U}$ has been used to calculate the mass bias and apply a correction for $^{240}\text{Pu}/^{239}\text{Pu}$. The fractionation factor, which was used to correct for the mass bias on $^{240}\text{Pu}/^{239}\text{Pu}$ ratio, was calculated based on the $^{235}\text{U}/^{238}\text{U}$ ratio (set at 0.0072527). After an acid blank correction, a linear regression through the half mass 239.5 and 240.5 was also made, to calculate the tailing on ^{239}Pu and ^{240}Pu .

Lab E: An ICP-SFMS (Element 2, Thermo) was used only for U isotopic ratio measurement. The sample introduction system included an SC2 DX auto sampler (Elemental Scientific) with prepFAST 400 online dilution system, PFA nebulizer, PFA cyclonic spray chamber with Peltier cooling from ESI, and sapphire demountable torch. Al skimmer and sample cones were used for the measurement. The typical sensitivity was approx. 0.8 cps per ppq for ^{238}U . ^{235}U and ^{238}U were measured in analog mode, and ^{234}U was measured in counting mode. The UH^+ formation at $m/z=236$ from ^{235}U was approx. 0.01%. For mass bias correction, IRMM-184 was used with appropriate concentrations versus tested sample.

Lab F: An ICP-QQQ (Agilent 8800) with a quartz Micromist nebulizer and a Peltier cooled (2°C) Scott double pass spray chamber was used for the analysis of both Pu and U. Because there was still U present in the sample solution after the single step extraction chromatography, mass was shifted to $m+16$ and $m+32$ through reaction with 0.32 mL/min CO_2 in the reaction cell, allowing for unreacted Pu to be analysed on mass (here: 239, 240, 242) with negligible remaining $^{238}\text{UH}^+$ interference. The concentrations of U are, in all samples, estimated at $m+16$ for control of the $^{238}\text{UH}^+$ interference. No correction equation was applied to the results, as the concentrations of U were low. The octapole bias was kept close to zero (-1 V) to prevent increased formation of PuO^+ . For increased sensitivity, an s-lens was used and the mass balance of the quadrupoles was set

to 92 % (240 amu/260 amu). Typical sensitivity in no-gas mode is about 1.5 cps per ppq for ^{238}U . Due to bureaucratic difficulties, it proved impossible to obtain an isotopic Pu standard for isotope calibration and mass bias determination. Therefore IAEA 135 certified reference material was chosen to be used as an isotopic standard material for mass bias correction based on the average $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio (n=47) published in literature. The concentrations of ^{239}Pu and ^{240}Pu were calculated from $^{240}\text{Pu}/^{242}\text{Pu}$ and $^{239}\text{Pu}/^{242}\text{Pu}$ multiplied by total amount of ^{242}Pu spiked.

Due to high concentrations of U in the sample, the instrument was run in low sensitivity mode and with x-lens installed. The samples were analyzed in MS-MS mode, where Q1=Q2, and with no gas present in the reaction cell. NBL CRM 129A was used for mass bias correction for the uranium atom ratios.

Quality control

The six laboratories in this inter-comparison exercise are leading Nordic laboratories with respect to ICP-MS and radiochemistry. Each lab in this inter-comparison exercise has well-established quality assurance program, as well as substantial experiences in operating ICP-MS measurement and relevant radiochemical separation for Pu and U. All the laboratories regularly participate into intentional inter-comparison exercise arranged by IAEA, NPL, IRMM and other organisations, and carry out internal performance evaluation by measuring certified reference materials. Most labs also perform U and Pu determination on a routine base and receive internal/external inspection for their quality control program.

Individual laboratory performance evaluation and scoring

Based on the ISO 13528 (ISO 13528) and IUPAC-CITAC recommendation [35], two tests including z-score and zeta-score were used to evaluate the individual performance of individual laboratory. z-score is calculated according to the following equation:

$$z = \frac{x - \bar{x}}{\sigma_t} \times 100\% \quad (1)$$

where x is the participant's result, X is the assigned value, σ_t is the standard deviation set externally for the performance assessment. The standard deviations (σ_t) were set to be 0.05 X for $^{234}\text{U}/^{235}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios, 0.005 X for $^{235}\text{U}/^{238}\text{U}$ atomic ratio and 0.2 X for ^{239}Pu and ^{240}Pu activity. According to the IUPAC-CITAC recommendation [35], the performance is considered to be acceptable if $|z| \leq 2$. A $|z|$ from 2 to 3 indicates that the results are of questionable quality. If $|z| > 3$, the analysis was considered to be out of control.

Optimally, according to the ISO 13528 standard for profession testing [35, 36], the *zeta*-score methodology should be used in evaluation of results in an inter-comparison. The *zeta*-score is calculated according to:

$$zeta = \frac{x - X}{\sqrt{u_x^2 + u_X^2}} \quad (2)$$

where x is the participant's result, X is the assigned value, u_x is the standard uncertainty of a participant's result, and u_X is the standard uncertainty of the assigned value. The performance is considered to be acceptable if $|zeta| \leq 2$. A $|zeta|$ from 2 to 3 indicates that the results are of questionable quality. If $|zeta| > 3$, the analysis was considered to be out of control.

Besides z -score and *zeta*-score, the relative bias was also calculated for evaluation of the analytical accuracy:

$$Bias = \frac{x - X}{X} \times 100\% \quad (3)$$

where x is the participant's result, X is the assigned value.

The criteria for accuracy evaluation is according to IAEA recommendation [37]. If the $|Bias| < MARB$ (Maximum Acceptable Relative Bias) the result will be 'Acceptable' for accuracy. In this inter-comparison, The MARB value was set to 10% for U isotopic ratios and 20% for $^{239, 240}\text{Pu}$ activities and $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio analysis, respectively.

Results and discussion

The results achieved from the inter-comparison exercise are presented in Table 2 for U isotopic ratios ($^{234}\text{U}/^{235}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$) in the NBL CRM 103-A reference material, and in Table 3 for Pu isotopes (^{239}Pu and ^{240}Pu) massic activity and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio in the reference material IAEA-384. The value of n in bracket is the number of replicates for the individual ICP-MS measurement. All uncertainties for the results obtained in this work are expanded uncertainties as obtained after uncertainty propagation with a coverage factor $k=1$.

U isotopic ratio

Six results were reported for U isotopic ratios in NBL CRM 103-A. However, as the reference material used for this inter-comparison is not certified, there is no value available, either for X or u_X . As the reference material used is of natural U composition, the IUPAC observed range of natural variations for U could be used (0.00725-0.00726 molar ratio) [25]. Because the number of participants in this inter-comparison is very small, we used the average of the IUPAC observed range of natural variations given in the publication, and the standard deviation for the upper and lower level of the range.

$^{234}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ atomic ratios: As depicted in Fig. 1 and 2, it can be seen that all the $^{234}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ atomic ratios obtained in this inter-comparison are within the range of natural variation of natural U. The absolute values of z -score and $zeta$ -score obtained for all results are less than 2, indicating the reported values and uncertainties are acceptable. All the laboratories achieved satisfactory accuracy both $^{234}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ atomic ratios with relative bias ranging from -1.0% to 1.6% (except Lab E obtained relative bias of about -6%).

$^{235}\text{U}/^{238}\text{U}$ atomic ratio: The recommended range of natural U is relatively narrow (0.00725-0.00726 molar ratio), some of the reported results (Lab C and Lab D) deviated from that range (Fig. 3(a)). All the z -score values are within ± 2 (Fig. 3(b)), indicating that all results meet the quantitative requirement (σ_t) set for this inter-comparison. However, in the $zeta$ -score test, two values of $|zeta|$ are in between of 2 and 3 (Lab

C=2.68, Lab D=2.28). This may be due to some bias was not taken into consideration when calculating the isotope ratio or the uncertainty. Nevertheless, high accuracy was obtained in all laboratories for $^{235}\text{U}/^{238}\text{U}$ atomic ratio with relative bias varying from -0.9% to 0.5%.

Pu concentration and isotopic ratio

Five results were reported for the Pu isotopes results for both pre-purified and the raw IAEA-384 material. In the pre-purification of Pu from IAEA-384 for direct measurement by ICP-MS by participating Labs, removal of U was deliberately retained insufficient (decontamination factor < 1000), in order to evaluate the performance of each laboratory in correcting for the polyatomic ions and tailing effect of ^{238}U at $m/z=239$ and 240.

^{239}Pu and ^{240}Pu massic activity: All the ^{239}Pu and ^{240}Pu values obtained for the pre-purified material in this inter-comparison are higher than the reference value, with relative bias within 8-17% (except ^{240}Pu results in Lab C, D and F with 31%, 187% and 26%, respectively) and most of them are even above the upper limit of the 95% confidential interval (Fig. 4(a) and 5(a)). All the ^{239}Pu and ^{240}Pu results obtained for the raw material are lower than the reference value, but well within the 95% confidential interval with relative bias of -13% to 8%. This indicates satisfactory accuracy for ^{239}Pu and ^{240}Pu massic activities was achieved in all the laboratories for the raw IAEA-384 material, while most results (except ^{240}Pu values reported by Lab C, D and F) for the pre-purified material have satisfactory accuracy.

From the results presented, it is expected that z -score and $zeta$ -score tests (Fig. 4 and 5) would result in positive values for the purified material, while tests for the raw material would result in negative values. All the results passed the z -score and $zeta$ -score tests for ^{239}Pu massic activity, indicating acceptable values and uncertainty (Fig. 4(b) and 4(c)). It can be seen from Fig. 5(b) that, except the Lab D result (9.37) for the pre-purified material which fails the z -score test, all the other z -score values for ^{240}Pu are distributed within the acceptance criteria. In the $zeta$ -score test (Fig. 5(c)), the $zeta$ -score for the Lab C result in pre-purified material is 2.87, indicating the ^{240}Pu value obtained is of questionable quality. This might be a consequence of the relatively low uncertainty for

the reported results. The *zeta*-score of the result of ^{240}Pu in pre-purified material reported by Lab D is 3.29, indicating that the analysis is considered to be out of control.

The difference in the overall results between pre-purified and raw IAEA-384 could be potentially due to the uncertainties existed in the concentrations of ^{242}Pu tracers and/or the inhomogeneity of the reference material. Another possible explanation to the consistent positive bias of the results for the pre-purified Pu samples could be due to the interferences (e.g., lanthanides [38]) present in the solution due to insufficient chemical separation. However, this explanation needs to be confirmed by further studies.

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio: The reference value for the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio for IAEA-384 is 0.049 ± 0.001 [39]. All the reported values in this inter-comparison (except the result for the raw IAEA-384 material in Lab D with an exceptionally high relative bias (144.9%)) meet the criteria for accuracy evaluation with relative bias from -10% to 8%. For the raw material, except Lab D that obtained a *z*-score of -2.04, all the other *z*-score and *zeta*-score values obtained by each individual lab meet the criteria of the acceptable performance (Fig. 6). However, for the purified material, results indicate some deviation: in the *z*-score test, one value (Lab F=2.45) is questionable and two values (Lab C=3.67 and Lab D=28.98) are unacceptable; in the *zeta*-score test, the Lab C and Lab D results (6.36 and 4.72, respectively) could be considered to be out of control. The high *zeta*-score obtained by Lab C for purified material might be related to the relative lower uncertainty in the reported results. The Lab D result of the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio for the pre-purified material that was out of control might be due to unexpectedly high tailing in the spectra from ^{238}U . The positive deviation from the reference value may be a result from not having control of the correction of the tailing at $m/z=240$ from ^{238}U . In this work, Lab D used a linear regression model for explaining the tailing from ^{238}U on the masses above. However, this model might not explain the tailing properly, thus under-correction of the spectral interference is plausible [40].

Uncertainty: Noteworthy is that the uncertainties for the Pu results, especially for ^{239}Pu , in the raw material for all laboratories are lower than for the pre-purified materials. This is most likely due to the fact that the pre-purified material was deliberately not

completely cleaned up so larger uncertainties in corrections for hydrides, tailing and various matrix effects could play a role. It might also be due to the limited amount of material distributed to each lab contains relatively low quantity of Pu in the solution, therefore the total count rate in ICP-MS would be lower than for the raw material prepared by individually.

Performance of different ICP-MS instruments

In this inter-comparison exercise, three ICP-SFMS, two ICP-QQQ and one MC-ICPMS instrument were used for the U isotopic ratio measurement. For the Pu concentration and isotopic ratio measurement, four ICP-SFMS and two ICP-QQQ were used for the inter-comparison exercise.

Precision for U isotopic ratio measurement

For U isotopic ratios measurement, Element XR ICP-SFMS at Lab C and MC-ICP-MS at Lab D obtained comparably high precision with the expanded relative uncertainties of 0.1-0.3%. The Lab B, Lab E and Lab F results are generally comparable within the range of 0.3-1.0%. Highest uncertainties were reported by Lab A ranging within 1.3-2.2%. It should be noted that for uncertainty estimation among all the laboratories in this work, the measurement precision of the sample as a main contributor, and the precision of the calibrator used for the correction of mass bias, the effect of dead time and the background have been taken into account.

In this work, all measurements using ICP-SFMS were done at low-resolution with maximum transmission and flat topped peaks to allow the best peak jumping conditions. The typical statistical precision for isotopic ratio measurement by double focusing ICP-SFMS instruments with single ion detection was reported to be about 0.1% [41], which is generally in line with the value reported by the ICP-SFMS at Lab C. Besides counting statistics, the measurement precision is affected by sample introduction and plasma fluctuation in the ICP source. The different introduction systems employed by ICP-SFMS instruments at Lab E (PFA-ST nebulizer) and Lab B (self-aspired nebulization with

conical nebulizer) could explain the difference in uncertainties obtained by the laboratories B, C and E.

ICP-SFMS and MC-ICP-MS are both sector field mass spectrometers with the application of single and multi-collector, respectively. The MC-ICP-MS has been reported in literature superior to the other instruments used with respect to isotope ratio measurements, provided that contribution from counting statistics is negligible. According to literature, one order magnitude higher precision can be achieved by MC-ICP-MS compared to ICP-SFMS [41]. The MC-ICP-MS enables flat-topped peaks even at higher resolution but drops in sensitivity. In this work, the MC-ICP-MS analysis was operated at low resolution mode with flat topped peaks at maximum transmission, therefore the relative uncertainty of the U isotope ratios measurement were superior (0.1-0.3%) to most single detector-ICP-MS results for U isotope ratios measurement in this work. The most likely reason for the relatively high uncertainty of U isotopic ratio measurement at Lab A relative Lab F (identical instrument with only the skimmer cone, Ni vs Pt, differs) is the daily performance.

Sensitivity and abundance sensitivity

Sensitivities for different ICP-MS instruments used in this work vary within 0.7-6 cps/ppq, with ICP-SFMS instruments (single or multi-collector) generally showing better transmission due to higher extraction voltage. Differences in sensitivity among different instrument types can be explained by different transmission efficiency, caused by differences in interface construction (e.g., ion deflection by ICP-QMS), acceleration voltages and electrostatic lens systems, vacuum systems, measurement strategies (reaction/collision mode) or mass resolution mode applied. Instruments equipped with improved interface design have yet an order of magnitude better transmission due to both geometry factors and the increased pumping rate. It is evident that the application of desolvation system APEX-Q at Lab C enhanced the sensitivity of ICP-SFMS instruments by 5 times (from 1.2 cps/ppq to 6 cps/ppq). The use of a high performance Pt cone and s-lens for ICP-QQQ at Lab F vs. Ni cone and x-lens at Lab A, led to a twofold increase in sensitivity.

The main problem in determination of ^{239}Pu and ^{240}Pu by ICP-MS is the occurrence of interferences, including peak tailing or abundance sensitivity effects of neighboring ^{238}U , and the formation of polyatomic ions. The pronounced polyatomic interferences are the formation of U hydrides ($^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^2\text{H}^+$) as the concentration of ^{238}U in most environmental samples is more than five orders of magnitude higher than that of ^{239}Pu and ^{240}Pu . Other nuclides in the sample matrix can also form polyatomic ions (e.g., $^{204}\text{Pb}^{35}\text{Cl}^+$, $^{207}\text{Pb}^{16}\text{O}_2^+$, $^{202}\text{Hg}^{37}\text{Cl}^+$, $^{208}\text{Pb}^{16}\text{O}_2^+$, $^{208}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$, $^{194}\text{Pt}^{14}\text{N}^{16}\text{O}_2^+$) which hamper the accurate detection of ^{239}Pu and ^{240}Pu [5, 42]. Therefore, careful chemical separation is necessary to eliminate these interferences, especially U, to ensure the reliability of the measurement.

Although most U in the sample can be removed effectively through several stages of chemical separation, a minor amount of U may always remain in the final solution before ICP-MS measurement. Application of proper sample introduction system in ICP-MS measurement for Pu measurement can efficiently reduce the UH^+/U^+ ratio. Cao et al. [42] summarized the interference effect from $^{238}\text{UH}^+$ by ICP-MS with different introduction systems reported in literature with UH^+/U^+ ratios varying from 1.5×10^{-3} to 7.2×10^{-6} . APEX-Q was reported to have one order of magnitude lower UH^+/U^+ ratio than pneumatic nebulizers such as MicroMist and PFA. In this work, however, APEX-Q system employed in combination with PFA nebulizer for ICP-SFMS at Lab C, indicated no better UH^+/U^+ ratio (10^{-5}) compared with the ICP-QQQ at Lab A and ICP-SFMS at Lab B (equipped with Conical nebulizer through self-aspired nebulization).

The quadrupole instruments have their main advantage in superior abundance sensitivity, which in particular is valid for the ICP-QQQ instrument using two quadrupoles thus enabling abundance sensitivities in the order of 10^{-14} . The ICP-QQQ further has a gas reaction cell enabling active removal of polyatomic interferences but at a cost in ion-transmission. In this work, a reaction cell was applied to the ICP-QQQ at Lab F to eliminate the ^{238}U interferences by highly efficient reaction of U^+ and UH^+ with CO_2 , but no reaction with Pu^+ .

576 It should be noted that even though this work focus much on the performance of different
577 ICP-MS instruments in the intercom-prison exercise, the difference in the analytical
578 accuracy and precision among the participating labs could also be related to different
579 sample processing procedure prior to the ICP-MS measurement, for example, whether a
580 microwave digestion procedure, filtering or a fusion melt was utilized in the sample pre-
581 treatment.

582 **Table 1** Instrumentation conditions used in each laboratory for the inter-comparison exercise

	Lab A	Lab B		Lab C		Lab D		Lab E	Lab F
Instrument model	Agilent 8800 ICP-QQQ	Element XR ICP-SFMS		Element XR ICP-SFMS		Nu Plasma MC-ICP-MS	AttoM double-focusing ICP-SFMS	Element 2 ICP-SFMS	Agilent 8800 ICP-QQQ
Radionuclides measured	^{234}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , ^{242}Pu	^{234}U , ^{235}U , ^{238}U	^{238}U , ^{239}Pu , ^{240}Pu , ^{242}Pu	^{234}U , ^{235}U , ^{238}U	^{239}Pu , ^{240}Pu , ^{242}Pu	^{234}U , ^{235}U , ^{238}U	^{239}Pu , ^{240}Pu , ^{242}Pu , ^{238}U	^{234}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , ^{242}Pu	^{234}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , ^{242}Pu
Auto-sampler	AS X-520 (CETAC))	No	No			ASX110	ASX260	SC2 DX	AS X-520 (CETAC))
Sample uptake	Peristaltic pump	Self-aspired nebulization	Self-aspired nebulization	Peristaltic pump	APEX-Q	Peristaltic pump	Peristaltic pump	PrepFast system	ISIS 2
Nebulizer	MicroMist (Borosilicate glass)	Conikal nebulizer	Conikal nebulizer	MicroMist nebulizer	PFA nebulizer	Meinhard and Desolvating nebulizer (DSN)	Meinhard nebulizer	PFA-ST	MicroMist quartz
Spray chamber	Quartz, , Scott-type double-pass	Twister spray chamber	Twister spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Cyclonic double pass spray chamber	Quartz baffled micro cyclonic with dual gas inlet	Quartz, Scott-type double-pass
Cooling	Peltier cooling system	No cooling	No cooling	No cooling	No cooling	No cooling	No cooling	PC ^{3x} -Peltier cooling system	PC ^{3x} -Peltier cooling system
Sample cone	1mm diameter orifice, Ni sample cone	Ni sampler, TF1001-Ni	Ni sampler, TF1001-Ni	Ni sample cone	Ni sample cone	Ni sample cone	Ni skimmer cone	Alunium ES-3000-18032	1 mm Pt cone
Skimmer cone	0.4 mm diameter orifice, stainless steel base with Ni tip	Ni skimmer, TF-1002A-Ni	Ni skimmer, TF-1002A-Ni	X skimmer cone	X skimmer cone	Ni skimmer cone	Ni skimmer cone	Alunium type X-Skimmer ES-3000-1805X	0.4 mm Ni skimmer cone,
RF generator	1500 W	1200 W	1200 W	1400 W	1400 W	1300 W	1300W	1350 W Power	1550 W
Typical sensitivity, cps/ppq ^{238}U	0.7	2	1.8	1.2	6	2	2	0.8	1.5 with s-lens (s-lens for Pu and x-lens for U)
$^{238}\text{U}^{\text{H}+}/\text{U}^+$	1/14892	1/104000	1/104000		1/100000		3/100000		None

583 **Table 2.** Results of U isotopic ratios for NBL CRM 103-A from each laboratory for the inter-comparison exercise (U is the expanded
584 relative uncertainty with a coverage factor of $k=1$)

Atom ratio		Lab A	LAB B	Lab C	Lab D	Lab E	Lab F	Ref. value
²³⁴ U/ ²³⁵ U	Average	0.007530 (n=10)	0.007672 (n=6)	0.007630 (n=6)	0.007587 (n=2)	0.007119 (n=6)	0.007490 (n=10)	0.007567
	<i>U</i> (<i>k</i> =1), %	1.63	0.64	0.20	0.22	0.64	0.47	8.20
	Bias, %	-0.49	1.38	0.83	0.26	-5.93	-1.02	
²³⁵ U/ ²³⁸ U	Average	0.007193 (n=10)	0.007268 (n=6)	0.007225 (n=6)	0.007278 (n=2)	0.007288 (n=6)	0.00727 (n=10)	0.007255
	<i>U</i> (<i>k</i> =1), %	1.36	0.30	0.14	0.12	0.36	0.37	0.07
	Bias, %	-0.85	0.18	-0.41	0.31	0.45	0.21	
²³⁴ U/ ²³⁸ U	Average	0.0000542 (n=10)	0.0000558 (n=6)	0.0000551 (n=6)	0.0000551 (n=2)	0.0000519 (n=6)	0.0000544 (n=1)	0.0000549
	<i>U</i> (<i>k</i> =1), %	2.21	0.72	0.18	0.31	0.96	0.55	8.20
	Bias, %	-1.28	1.64	0.36	0.55	-5.56	0.91	

585

586 **Table 3.** Results of Pu isotopes for IAEA-384 from each laboratory for the inter-comparison exercise (U is the expanded relative
587 uncertainty with a coverage factor of $k=1$)

Institute	Lab A		Lab B		Lab C		Lab D		Lab F		Ref. value
Sample name	Pre-purified Pu (n=5)	Raw material (n=2)	Pre-purified Pu (n=1)	Raw material (n=3)	Pre-purified Pu (n=5)	Raw material (n=2)	Pre-purified Pu (n=1)	Raw material (n=1)	Pre-purified Pu (n=3)	Raw material (n=2)	Raw material
²³⁹ Pu, Average	106.0	89.4	107.3	85.4	108.6	86.3	115.4	96.6	110.0	95.0	98 (85-105)
Bq/kg											
$U (k=1), \%$	2.1	0.8	1.6	0.8	1.5	1.3	16.5	5.3	6.1	2.0	
Bias, %	8.2	-8.8	9.5	-12.9	10.8	-11.9	17.8	-1.4	12.2	-3.1	
²⁴⁰ Pu, Average	20.3	16.6	20.5	15.8	22.9	15.8	50.3	15.9	22.0	18.3	17.5 (15.1-18.7)
Bq/kg											
$U (k=1), \%$	15.8	3.0	2.0	1.3	3.1	2.5	19.5	21.4	8.2	1.6	
Bias, %	16.0	-5.1	17.0	-9.7	30.9	-9.7	187.4	-9.1	25.7	4.6	
²⁴⁰ Pu/ ²³⁹ Pu Average	0.053	0.051	0.052	0.050	0.058	0.050	0.120	0.044	0.055	0.053	0.049
atom ratio											
$U (k=1), \%$	13.2	3.9	13.5	10.0	1.7	2.0	12.5	11.4	5.5	3.8	2.0
Bias, %	8.2	4.1	6.1	2.0	18.4	2.0	144.9	-10.2	12.2	8.2	

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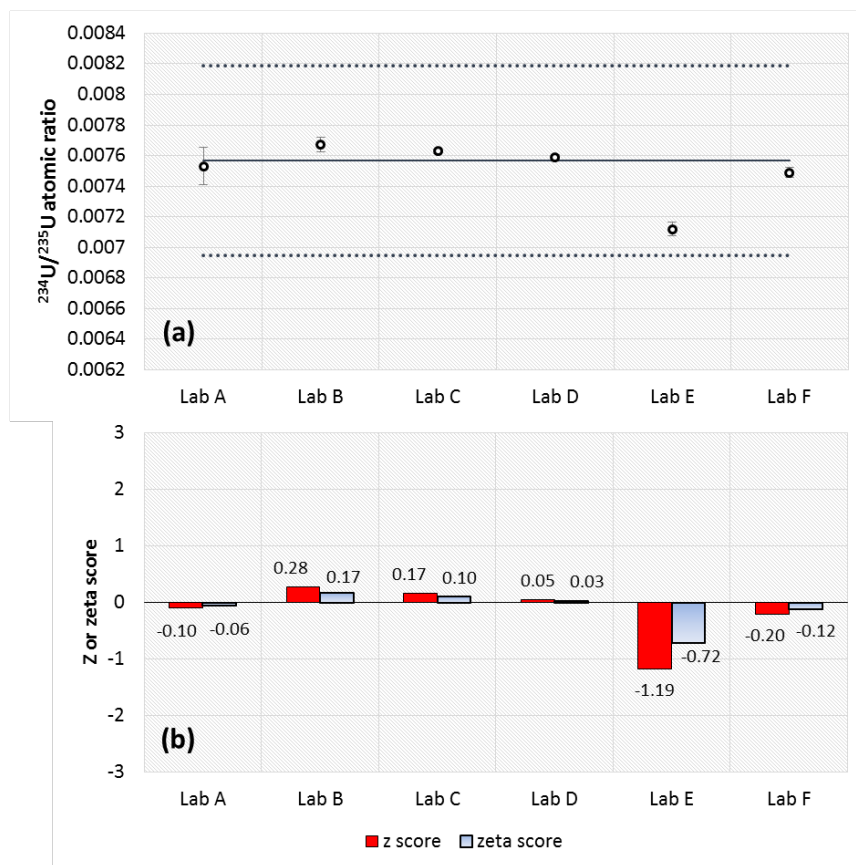


Fig. 1 $^{234}\text{U}/^{235}\text{U}$ isotope ratio (a) and z-score and zeta-score (b) calculated from the measurement of the reference material NBL CRM 103-A. The solid and dotted lines represent the observed average and variation of natural U (given by IUPAC), respectively [25]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.

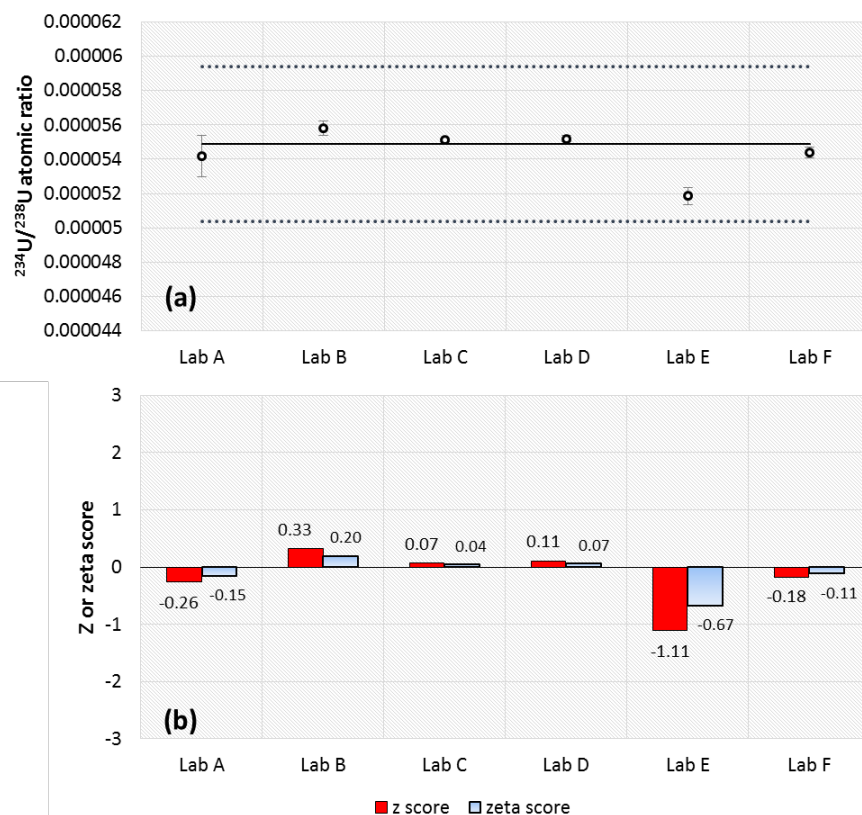


Fig. 2 $^{234}\text{U}/^{238}\text{U}$ isotope ratio (a) and z -score and $zeta$ -score (b) calculated from the measurement of the reference material NBL CRM 103-A. The solid and dotted lines represent the observed average and variation of natural U (given by IUPAC), respectively [25]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.

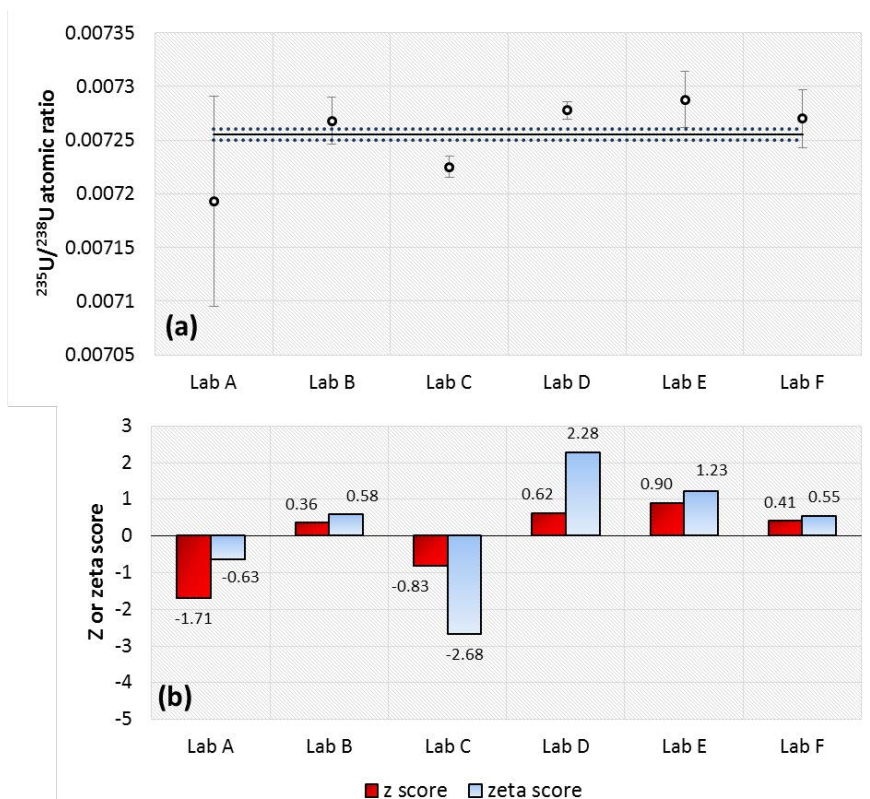


Fig. 3 $^{235}\text{U}/^{238}\text{U}$ isotope ratio (a) and z -score and $zeta$ -score (b) calculated from the measurement of the reference material NBL CRM 103-A. The solid and dotted lines represent the observed average and variation of natural U (given by IUPAC), respectively [25]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.

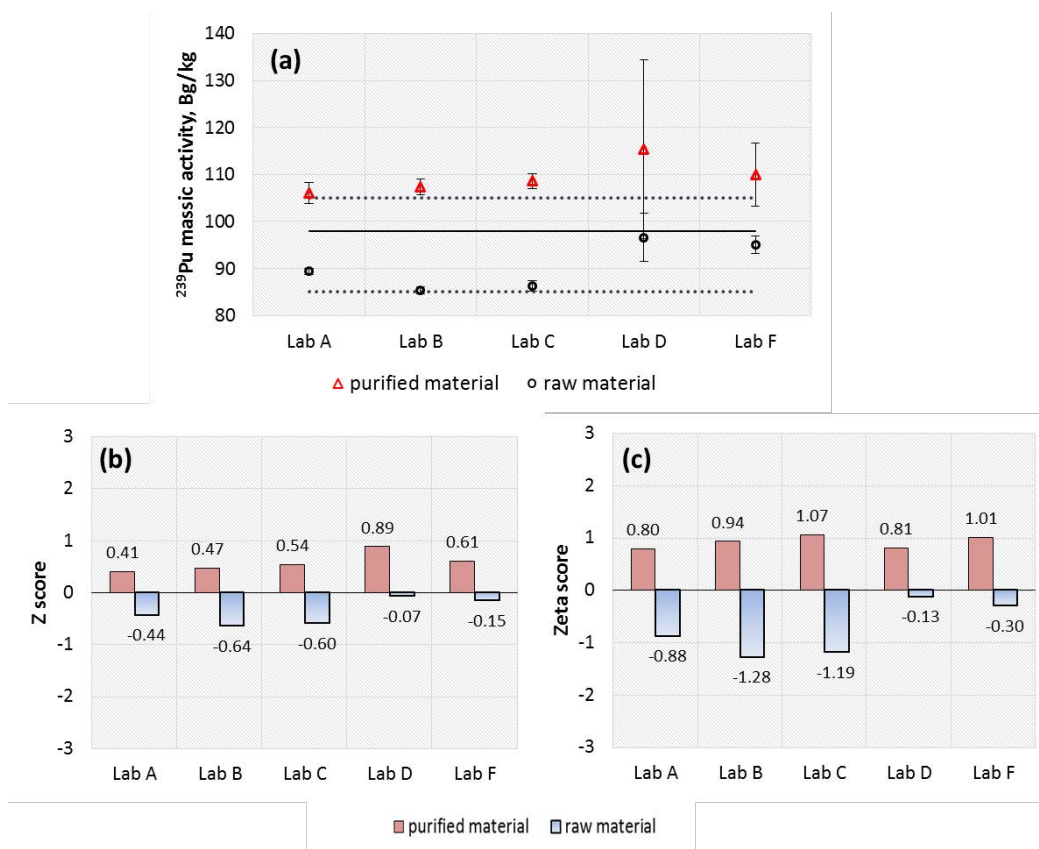


Fig. 4 ^{239}Pu massic activities (a), Z-score (b) and Zeta-score (c) for the reference material IAEA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval [39]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.

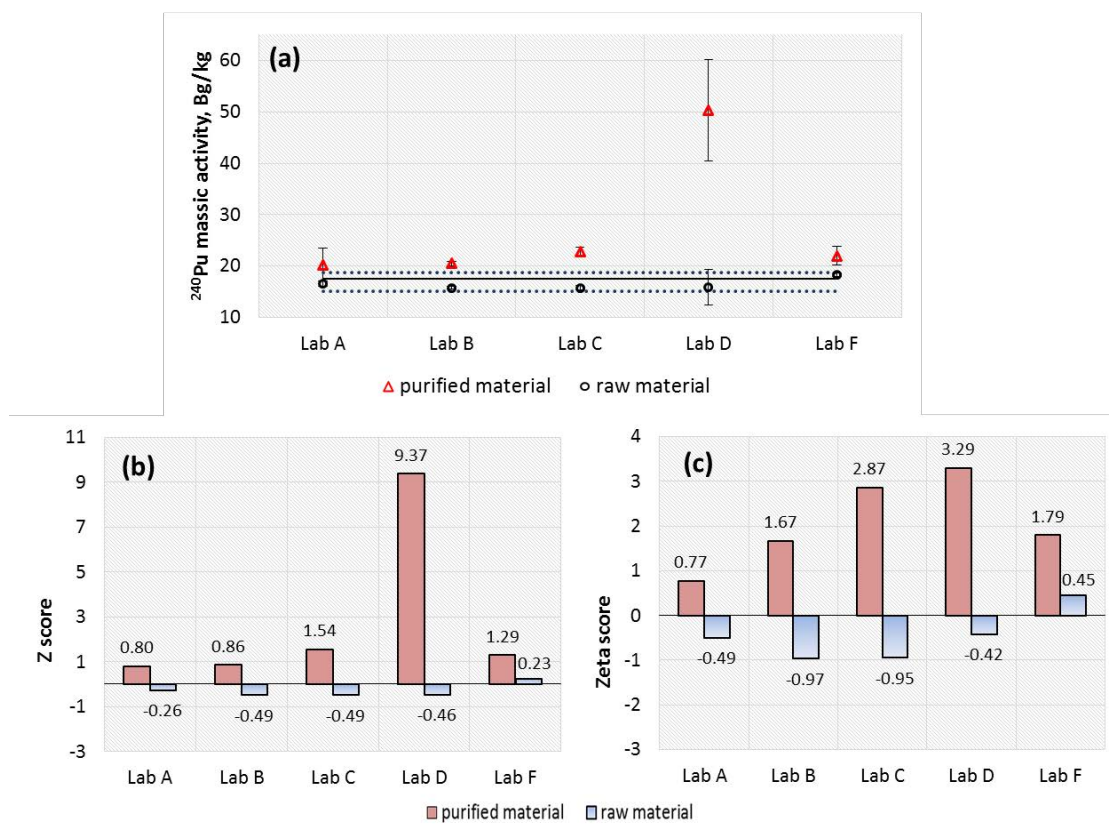


Fig. 5 ^{240}Pu massic activities (a), Z-score (b) and Zeta-score (c) obtained for the reference material IAEA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval [39]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.

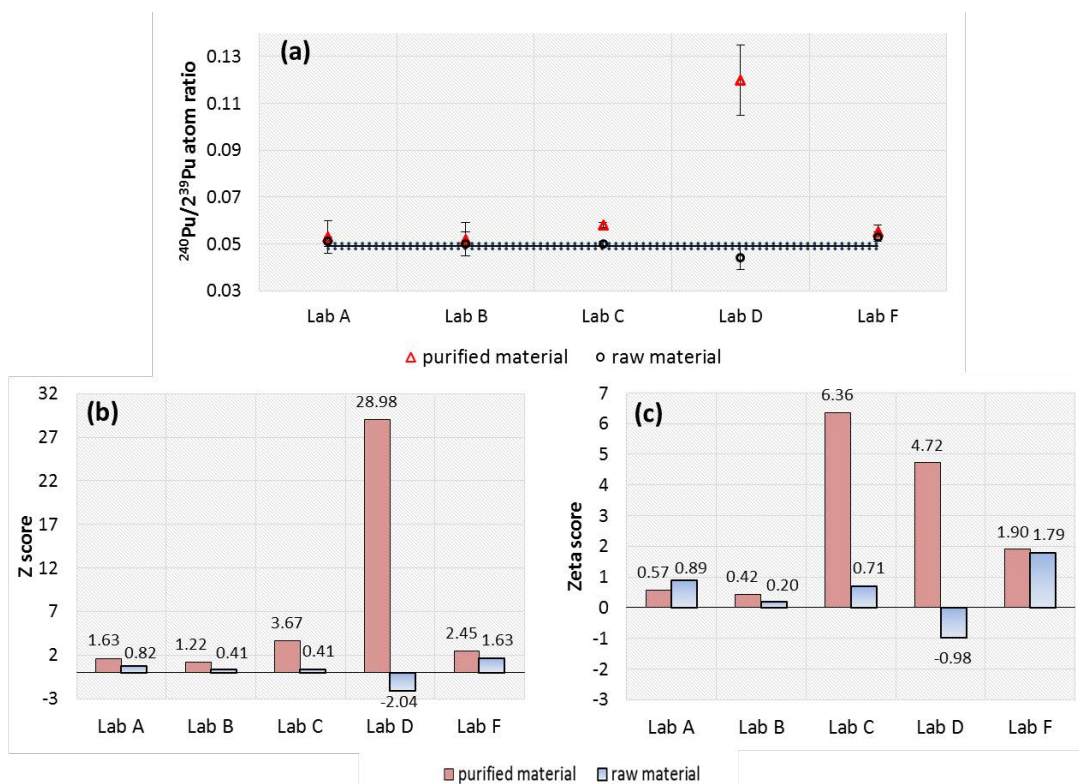


Fig. 6 $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio (a), Z -score (b) and $Zeta$ -score (c) obtained for the reference material IAEA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval [39]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.

Conclusions

Satisfactory accuracy was obtained in this inter-comparison exercise for all the U isotopic ratio measurement. High-resolution sector field ICP-MS is the preferred option to achieve high precision for U isotopic ratios. Although the U isotopic ratios measurement for NBL103 A was generally well performed in all labs, the measurement precision obtained in this work leaves room for improvement.

All the Pu results reported for the raw IAEA-384 material achieved satisfactory accuracy, while few ^{240}Pu values for the pre-purified material indicate high relatively bias. This emphasizes the importance of the purity of Pu fraction with respect to the analytical accuracy and special care needs to be paid on the existence of interfering nuclides which could possibly induce large analytical error in the measurement. If the ICP-MS is sensitive to matrix effect or a solely calibration would not ensure the accuracy of the Pu result measured from a non-purified solution, an additional chemical purification of the Pu fraction might be needed.

It is believed that this inter-laboratory exercise is beneficial to share among different ICP-MS users and prompt more efficient application of ICP-MS. The fact of no satisfactory explanations on the lack of accuracy for some results obtained in this inter-comparison supports the idea that inter-comparisons should be conducted repeatedly to identify trends among laboratories.

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